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Background Information for Establishment of National Standards of Performance for New Sources

Castor Bean Processing

Walden Research Corp.

prepared for
Environmental Protection Agency

JULY 1972

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RESEARCH CORPORATION

BACKGROUND INFORMATION FOR ESTABLISHMENT OF NATIONAL STANDARDS OF PERFORMANCE FOR NEW SOURCES

CASTOR BEAN PROCESSING

Contract No. CPA 70-165
Task Order No. 7

Walden Research Corporation
Cambridge, Massachusetts

Prepared for

Division of Applied Technology
Office of Air Programs
Environmental Protection Agency
Research Triangle Park, North Carolina

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16. Abstracts

Castor oil is one of the more important vegetable oils being used industrially. This report presents background information for this new source of pollutant emission. Section 2 presents the economic and statistical background which includes castor oil production facilities, Section 3 discusses production methods and processes which include seed handling, castor pomace processing, and oil refining. The uses of castor oil and castor oil products are discussed in Section 4. Section 5 deals with the industrial emissions. Mainly particulates and emissions from oil refining. The final section discusses control technology: dry particulate collectors, wet scrubbers, adsorption, and incineration.

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1. INTRODUCTION

1.1 GENERAL

Castor oil is one of the more important vegetable oils being used industrially, even though, in terms of volume, it ranks low among other oils (Table 1-1) [1]. The castor oil has many unique properties, and is capable of undergoing several kinds of chemical transformations, resulting in desirable derivative substances (dehydrated, sulfonated, sulfated, hydrogenated, and blown castor oil). The following excerpt from a Baker Castor Oil Bulletin [2] describes the special nature of the oil.

> Castor oil is obtained from the seeds of Ricinus Communis, a plant that grows readily in most tropical and sub-tropical areas. As the result of an extensive agronomic research program undertaken by this company in cooperation with the U.S. Department of Agriculture, the castor plant is now grown commercially in the United States. Castor oil is a versatile chemical and is used as the starting material for a wide variety of technical and commercial products. Its unusual chemical composition facilitates the conversion of castor oil into numerous derivatives.
>
> Castor oil is a triglyceride (ester) of fatty acids. Approximately 90% of this fatty acid content is ricinoleic acid, an 18-carbon acid having a double bond in the 9-10 position and a hydroxyl group on the 12th carbon. This combination of hydroxyl group and unsaturation exists only in castor oil. The composition of castor oil fatty acids, which is remarkably constant, is shown below:
>
> | | |
> |---|---|
> | Ricinoleic Acid (12-hydroxy oleic) | 89.5% |
> | Dihydroxystearic Acid | 0.7 |
> | Palmitic Acid | 1.0 |
> | Stearic Acid | 1.0 |
> | Oleic Acid | 3.0 |
> | Linoleic Acid | 4.2 |
> | Linolenic Acid | 0.3 |
> | Eicosanoic Acid | 0.3 |
>
> The hydroxyl groups in castor oil account for a unique combination of physical properties: relatively high viscosity and specific gravity; solubility in alcohols

TABLE 1-1

OILS, OILSEEDS AND FATS: ESTIMATED WORLD PRODUCTION ON OIL EQUIVALENT BASIS, AVERAGES 1935-54, ANNUAL 1954-65 1/

Commodity 2/	Average 1935-39 2/	Average 1945-49 2/	Average 1950-54 2/	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965 3/
	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.	Mil. lb.
Edible Vegetable Oils 4/															
Corn oil	---	---	---	---	---	316	330	340	380	390	420	450	480	490	530
Cottonseed	2,710	2,440	3,660	4,410	4,150	4,240	4,060	3,940	4,400	4,560	4,610	4,860	5,000	5,160	5,350
Peanut	3,130	3,760	3,550	3,780	4,070	4,280	4,780	5,140	5,200	4,650	4,790	5,040	5,410	5,610	6,100
Soybean	2,360	3,060	4,110	4,470	5,050	5,490	5,970	6,400	7,330	7,630	7,320	8,040	8,390	8,540	9,000
Sunflower Seed	1,850	1,660	1,930	2,200	1,730	2,820	3,120	2,740	3,780	3,150	3,980	4,370	5,060	4,350	5,740
Rapeseed	2,660	2,330	2,090	2,010	2,420	2,190	2,510	2,470	2,530	2,560	2,640	2,990	2,400	2,500	3,150
Sesame Seed	1,430	1,410	1,490	1,560	1,410	1,170	1,110	1,000	1,210	1,170	1,050	1,170	1,180	1,170	1,160
Safflowerseed	---	---	---	---	---	172	184	182	208	256	294	312	442	456	390
Olive Oil	1,950	1,834	2,160	2,600	2,170	1,640	2,400	2,500	2,410	2,600	2,960	2,950	2,070	3,730	2,150
Total	15,190	16,464	18,990	20,760	21,000	22,318	24,464	24,712	27,428	26,968	28,064	29,782	30,432	32,206	33,570
Palm Oils 5/															
Coconut	4,270	3,240	4,170	4,330	4,460	4,900	4,970	4,340	4,070	4,480	4,790	4,650	4,840	4,870	4,850
Palm Kernel	800	670	840	940	850	940	850	920	910	880	880	810	820	830	820
Palm	2,180	2,000	2,570	2,750	2,720	2,760	2,800	2,810	2,850	2,910	2,820	2,730	2,780	2,800	2,810
Babassu Kernel	50	70	102	90	106	80	102	114	106	132	140	150	154	160	170
Total	7,300	5,980	7,682	8,110	8,136	8,680	8,722	8,814	7,936	8,402	8,630	8,340	8,594	8,660	8,650
Industrial Oils 4/															
Linseed	2,290	2,200	2,020	2,060	1,950	2,180	2,810	2,200	2,250	2,150	2,230	2,160	2,310	2,380	2,310
Castor Bean	400	420	430	420	430	430	490	490	480	590	530	580	650	600	690
Oiticica	20	24	20	12	26	28	22	36	2	44	36	56	12	54	50
Tung	300	236	246	246	210	202	290	300	282	272	240	216	200	246	256
Perilla	130	10	10	12	8	10	10	10	12	12	10	12	10	8	4
Total	3,140	2,890	2,726	2,750	2,624	2,850	3,622	3,036	3,026	3,068	3,046	3,024	3,182	3,488	3,310
Animal Fats															
Butter (fat content) 7/	8,380	8/ 6,900	7,300	7,750	7,740	7,860	8,100	8,260	8,180	8,500	8,590	8,750	8,750	8,830	8,870
Lard 6/	5,380	6,200	6,350	6,880	6,950	7,300	7,220	7,640	8,160	8,000	8,090	8,170	8,130	7,690	7,800
Tallow and Greases	3,060	4,036	5,060	5,650	5,940	6,530	6,530	6,500	6,930	6,880	7,280	7,290	8,080	8,780	8,450
Total	16,820	17,136	18,710	20,280	20,630	21,690	21,850	22,400	23,270	23,380	23,960	24,210	24,960	25,300	25,120
Marine Oil															
Whale	1,090	560	880	910	840	850	880	870	834	836	856	780	590	498	410
Sperm Whale	60	80	160	160	200	240	220	270	260	244	240	260	298	320	290
Fish (Including liver)	960	550	940	1,040	892	912	768	768	950	1,022	1,338	1,434	1,364	1,578	1,690
Total	2,110	1,190	1,980	2,110	1,932	2,002	1,868	1,908	2,044	2,102	2,434	2,524	2,252	2,396	2,390
Estimated World Total	44,560	43,660	50,088	54,010	54,322	57,540	60,526	60,240	63,704	63,920	66,134	67,880	69,420	72,050	73,040

1/ Converted from data published by Foreign Agricultural Service in thousand short tons.
2/ For the averages 1935-39 and 1945-49, production refers to the years in which the seed was produced and not necessarily when the oil was extracted. Beginning with 1950-54 average, production refers to the years in which the predominant share of the given oil or fat, was produced from its related raw material.
3/ Preliminary.
4/ Estimates of U. S. oil production include actual oil produced plus the oil equivalent of exported oilseeds; estimates for other countries are based upon the production of various oilseeds times the estimated normal proportion crushed for oil.
5/ Estimated on the basis of exports and information available on production and consumption in the various producing areas.
6/ Rendered lard only in most countries.
7/ 1934-38 average.
8/ 1946-49 average.

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in any proportion; limited solubility in aliphatic petroleum solvents. The uniformity and reliability of its physical properties are demonstrated by the long-time use of castor oil as an absolute standard for viscosity tests. Because of its highly polar hydroxyl groups, castor oil is compatible with, and will plasticize, a wide variety of natural and synthetic resins, polymers, elastomers and waxes. It has excellent emollient and lubricating properties and a marked ability to wet and disperse dyes, pigments and fillers. In the form of its chemical derivatives, castor oil's application versatility is further enhanced.

The hydroxyl groups, double bonds and ester linkages in castor oil provide reaction sites for the preparation of many useful derivatives. Chemical reactions commercially used to create important castor oil derivatives are as follows:

Acetylation
Alkoxylation
Amination
Caustic Fusion
Chemical Dehydration
Epoxidation
Esterification
Hydrogenation
Isocyanate Reactions
Oxidative Polymerization
Pyrolysis
Saponification
Sulfation

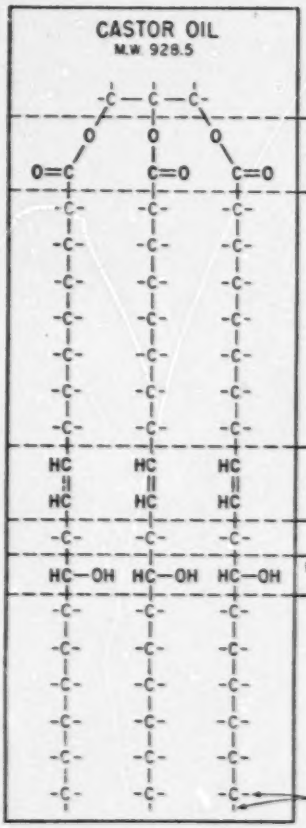
Figure 1-1 [2] diagrams the molecular structure of the castor oil and lists some of the chemical processes to which it may be subjected.

Castor pomace (meal and flour) is a by-product of the oil extraction process. A pound of castor seed has an approximate yield of a half a pound of pomace and a half a pound of oil. The pomace is generally used as a fertilizer, although its use as an animal feed has been attempted with some degree of success.

1.2 TOXICITY

The castor pomace contains a toxic protein called ricin, a slightly toxic alkaloid called ricinine, and an allergen. Ricin can be lethal but is easily detoxified.

All commercially-available imported pomace must be detoxified [3]. The oil does not contain any toxic ingredients, which instead remain in the press cake.



CHEMICAL REACTIONS OF CASTOR OIL

NATURE OF REACTION	ADDED REACTANTS	TYPE OF PRODUCTS
(1) Hydrolysis	Acid, enzyme, or Twitchell reagent catalyst	Fatty acids Glycerol
(2) Esterification	Monohydric alcohols	Esters
(3) Alcoholysis	Glycerol, glycols, pentaerythritol, etc.	Mono- and diglycerides, monoglycols, etc.
(4) Saponification	Alkalies Alkalies plus metallic salts	Soluble soaps Insoluble soaps
(5) Reduction	Na reduction	Alcohols
(6) Amidation	Alkyl amines, alkanolamines, etc.	Amine salts Amides
(7) Halogenation	$SOCl_2$	Fatty acid halogens
(8) Oxidative polymerization	Heat, air, oxygen	Polymerized oils
(9) Hydrogenation	Hydrogen (moderate pressure)	Hydroxystearates
(10) Epoxidation	Hydrogen peroxide	Epoxidized oils
(11) Halogenation	Cl_2, Br_2, I_2	Halogenated oils
(12) Addition reactions	S, maleic acid	Polymerized oils
(13) Sulfonation	H_2SO_4	Sulfonated oils
(14) Dehydration	Catalyst (plus heat)	Dehydrated castor oil
(15) Caustic fusion	NaOH	Sebacic acid Caprvl alcohol
(16) Pyrolysis	High heat	Undecylenic acid Heptaldehyde
(17) Halogenation	PCl_5, $POCl_3$	Halogenated castor oil
(18) Alkoxylation	Ethylene and/or propylene oxides	Alkoxylated castor oils
(19) Esterification	Acetic-, maleic-, phthalic anhydrides	Alkyl castor oils
(20) Amination	Oxidation plus NH_3	12-amino oleate
(21) Sulfation	H_2SO_4	Sulfated castor oil (Turkey red oil)
(22) Urethane reactions	Tolylene diisocyanate	Polymers

Figure 1-1. Castor Oil Structure and Derivatives.

1.3 PRODUCTION

The castor oil extraction procedure is similar to that used for most oilseeds but the presence of harmful materials require that greater care be taken in handling the seeds and in suppressing the dust [4]. Domestic cultivation of the castor plant has ceased for the time being at least. A combination of market prices, the end of the government support program, and the development of competitive products, virtually eliminated castor as a domestic farm crop [5]; the 1971 planting was about 4,000 acres -- with a yield about 2,000 tons of seed or perhaps a 20 day supply for an oil mill, which is completely uneconomical. In addition, major foreign growers, for reasons of balance of trade, have converted their facilities so that they can also extract and sell the oil, in some cases prohibiting export of seed.

Figure 1-2 [6] illustrates the trend away from importing castor seeds. The result of these two facts (no domestic crop and no seed imports) is the total absence of domestic seed crushing and oil extraction. In the summer of 1971 the last crushing operation stopped (the Plains Coop Oil Mill, Plainview, Texas). This operation utilized the seeds from local farms (which was the last domestic crop).

Thus, the United States castor industry is now almost entirely concerned with refining the imported oil into its derivative products, and with distribution of the oil. In addition, there is a large research effort designed to discover new markets for castor products because of continuing inroads both by other natural oils and by synthetic materials.

1.4 AVAILABILITY OF INFORMATION SOURCES

Available information in the castor industry has been limited to dated texts discussing the oil extraction processes, sketchy statistical data from the Bureau of the Census and the Department of Agriculture, and private communication with industry sources.

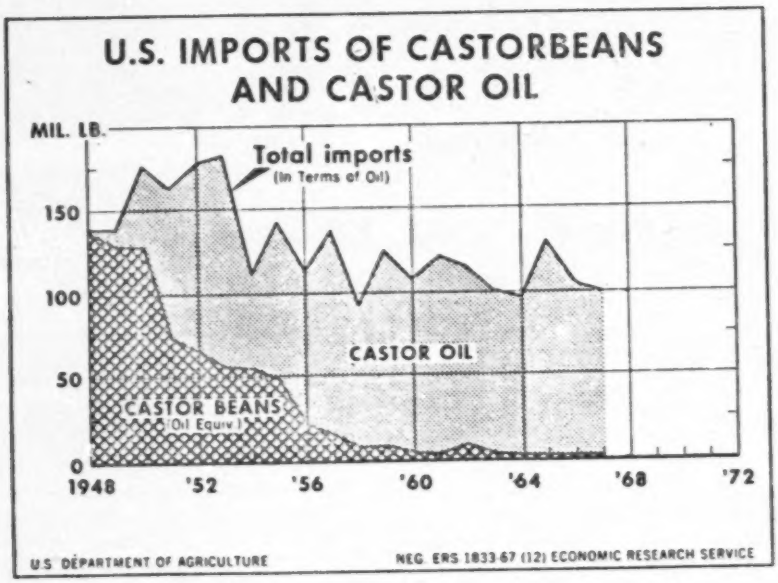

U.S. IMPORTS OF CASTORBEANS AND CASTOR OIL
MIL. LB.
Total imports
(In Terms of Oil)
150
100
50
0
CASTOR OIL
CASTOR BEANS
(Oil Equiv.)
1948
'52
'56
'60
'64
'68
'72
U.S. DEPARTMENT OF AGRICULTURE
NEG. ERS 1833-67 (12) ECONOMIC RESEARCH SERVICE

Figure 1-2

2. ECONOMIC AND STATISTICAL BACKGROUND

2.1 GENERAL

As indicated in the previous section, the domestic castor products industry is now almost exclusively concerned with distributing oil and with obtaining oil derivatives. There is also a trade in castor pomace which is of secondary importance. Brazil supplies the bulk of our castor oil imports with Japan supplying virtually the remainder. (In 1967 78% of our imports were Brazilian and 21% Japanese [6].)

The domestic consumption of castor products by use is shown in Figure 2-1. The industry breakdown shown in this figure is not precise and the only reliable number if the total consumption figure, although the industry breakdown does give some indication of the relative importance of the various users. The reasons for the lack of accuracy are due in part to the relatively small consumption of castor products, and in part to the Census Bureau's attempt to avoid disclosing figures of individual companies. The large number of end products and uses shown in Table 4-2 help explain the size of the "OTHER" category as the third largest consumption.

The oil and fat products market situation has required the castor products industry to invest extensively in research endeavors in an attempt to find new uses for castor derivatives. The competition has been such that a great many of the castor products customers of twenty years ago have now found suitable substitute products. The research effort has, therefore, been of vital importance in maintaining a constant level of sales [7].

The United States Government has had a castor seed price-support policy at various times in the past. Future prospects for effective price support programs in the industry appear dim.

2.2 PRODUCTION FACILITIES

2.2.1 Seed Crushing and Oil Extraction Plants

With the crushing of the final domestic castor seed crop at the Plains Coop facility, the last of these operations has come to an end. Interestingly, Mr. D. L. Van Horn, former agriculture consultant to the Plains Coop, states that the 4000-acre 1970 castor crop was purchased by the McNair Feed Company, which is arranging for its resale and export. Apparently, even the availability of this seed quantity is not sufficient to justify continued domestic crushing [8].

The only other operation known to be of recent vintage is that of the Pacific Vegetable Oil Co., located in Richmond, California. It is understood that this has not been in operation for some four to five years [9].

2.2.2 Oil Refining Facilities

Using the 1970 Paint Red Book [10] and the Chemical Materials Index [11], a list of companies handling castor products was made. These companies were contacted to determine the nature of the castor products they deal with. Table 2-1 is a list of companies contacted.

Baker Chemical Company is the largest castor oil refiner in the country, with Spencer-Kellogg second. Over half of the domestic castor products are supplied by these two firms.

2.2.3 Other Castor Product Facilities

All domestic castor oil and pomace originates from foreign sources (excluding Government stocks and material still remaining from very recent American crops). The distribution of the castor imports is accomplished by brokers or by large processors. For example, Brett Corporation (Table 2-1) is an import broker representing one Brazilian grower. Brett is concerned only with resale of the product. On the other hand, Baker Castor Oil Company is concerned principally

Figure 2-1. United States Consumption of Castor Oil.

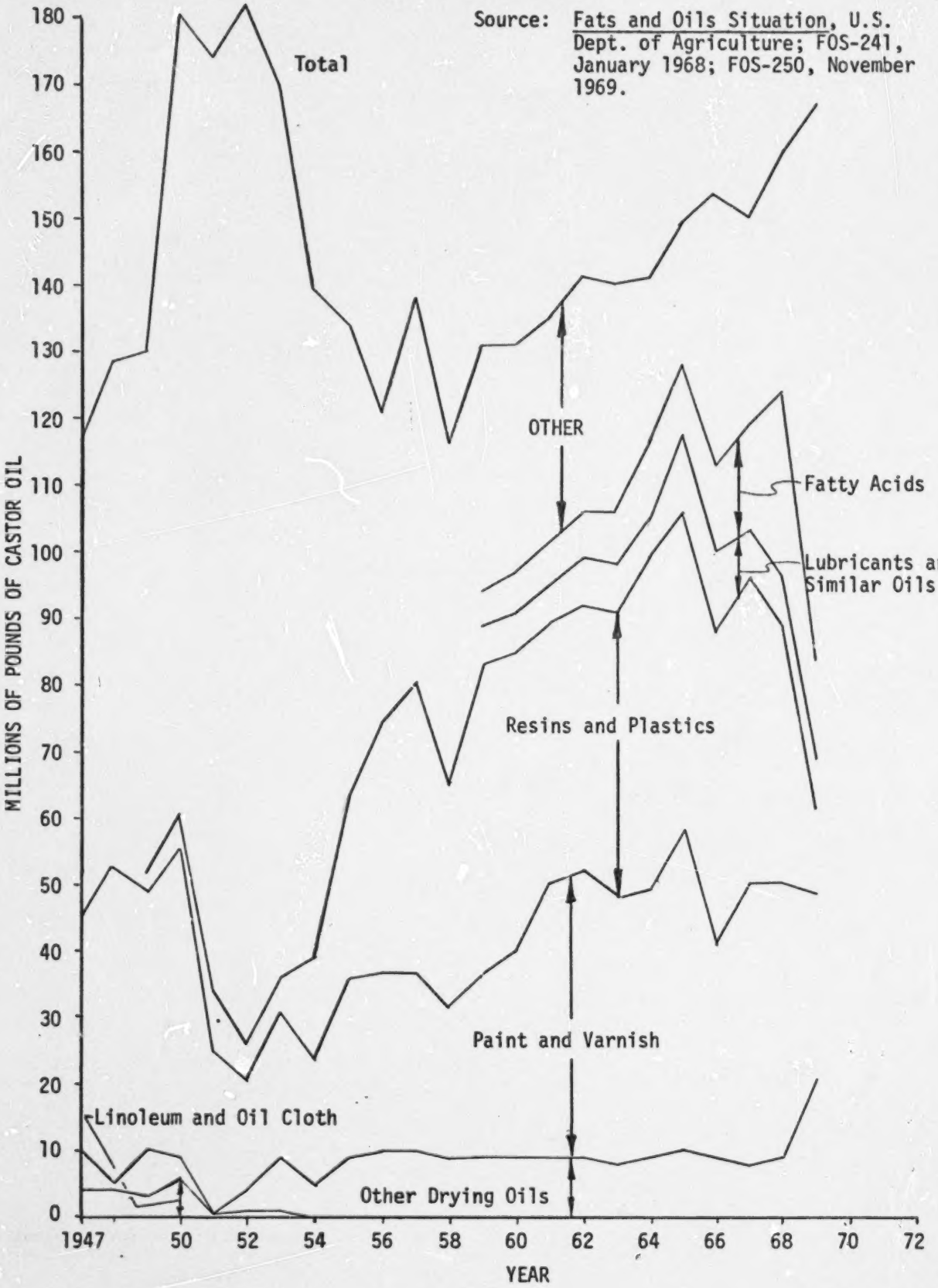


TABLE 2-1

CONTACT LIST

Company	Address	Telephone	Contact	Type of Castor Products Operation
Ashland Chemical Co.	Englewood Cliffs, N.J.	201-568-3023		Distributor only
Baker Castor Oil Co.	Bayonne, N.J.	201-436-8800	Mr. J. Paraskevas	Largest castor oil refiner
Brazilian Industrial Oils	New York, N.Y.	NA		Out of business, was broker only
Brett Corporation (Div. Hollingshurst)	New York, N.Y.	212-867-1035	Mr. Squires	Import and distribute only
Cadwell and Jones	E. Hartford, Conn.	203-289-9555	Mr. Gordon	Mix castor pomace in fertilizer
Capital City Products	Columbus, Ohio	614-299-3131		No longer handle castor products
Culbro Tobacco Co.	E. Hartford, Conn.	203-243-2561	Mr. R. Milliken Farm Manager	Use castor fertilizer
Degen Oil & Chem. Co.	Jersey City, N.J.	201-432-1192	Mr. Pollock	Esterification (∿ 400 F)
Drew Chemical Corp. (Div. Pacific Vegetable Oil)	Boonton, N.J.	201-887-9300	Mr. Retkua Bulk Oil Mgr.	Import only
Emery Industries, Inc.				No longer handle castor products
GAF Corporation	Linden, N.J.	212-582-7600	Mr. F. Krupin Product Mgr.	Sulfation; epoxidation (∿ 80-90 C)
Harchem (see Union Camp Corporation)				
Hercules, Inc.	Kalamazoo, Mich.	616-343-6161	Mr. J. B. Moniz Manager	Produce sulfonated oil

TABLE 2-1 (continued)

Company	Address	Telephone	Contact	Type of Castor Products Operation
Humko Products, Chemical Div.	Clifton, N.J.	901-682-9111	Mr. A. Cereghino Vice President	Produce fatty acids
Kerr McGee	W. Springfield, Mass.	413-739-4737	Mr. Cook	Mix castor pomace in fertilizer
Meyer & Mendelsohn	Windsor, Conn.	203-688-2734	Mr. Thomas Farm Manager	Use castor fertilizer
Old Fox Agricultural Sales	Hazardville, Conn.	203-749-8339	Mr. W. Williams Sales Manager	Mix castor pomace in fertilizer
Pacific Vegetable Oil Corp.	Los Angeles, Calif.	213-264-3904	Mr. S. Ross	Produce small amounts of blown oil and distribute crude oil
Plains Coop Oil Mill	Plainview, Texas	806-293-2604	Mr. D. Van Horn (with McNair Feed)	World's only modern castor bean mill, now phased out.
Polyester Corp.	Southampton, N.Y.	516-283-4400	Mr. J. Craker	Distribute only
Sherwin Williams Chem., Div. Sherwin Williams Co.				No longer handle castor products
Spencer Kellogg Div. Textron Inc.	Buffalo, N.Y. (Hdqtrs) Edgewater, N.J. (Plant)	716-852-5850	Mr. R. Hussong Prod. Super.	Second largest castor oil refiner
Union Camp Corp.	Dover, Ohio	216-343-7701	Mr. V. Bedrosian Plant Manager	Largest U.S. user of castor products
Woburn Chemical Corp.	Kearney, N.J.	201-991-3300	Mr. D. Fritz General Manager	Blend only, stopped making dehydrated oil in July 1971.

with refining a large portion of the imported oil which is sold as industrial products or various intermediates.

3. PRODUCTION METHODS AND PROCESSES

3.1 GENERAL

Most of the world's castor crop is hand-picked, although machine picking has been used domestically for a number of years. A large capital investment in equipment, plus the need for using a hybrid castor plant, have hindered the mechanization process abroad. Screw pressing is the most common oil extraction method in use. The continuous nature of its operation gives it a sizable advantage over hydraulic pressing. Solvent extraction is commonly used in conjunction with mechanical pressing to complete the oil removal process. The extracted oil is then processed to suit the product requirements, while the castor pomace, a by-product of the oil extraction procedure, is also prepared for marketing. Figures 3-1 and 3-2 are flow diagrams showing typical pre-pressing and solvent extraction.

The following sections describe the basic production procedures. Much of this information was obtained from data of the Plains Coop Oil Mill in Plainview, Texas [8], which is apparently the only modern castor processing mill in the world. This mill is in the process of shutting down its castor operation for lack of seed as indicated above.

3.2 SEED HANDLING

The historical trend in the castor industry has been to locate the crushing mills in the castor growing areas which explains the siting of the Plainview mill. The seeds are transported directly to the mill from the local farms while seed producers in other areas utilize receiving stations set up to facilitate rail or truck deliveries to the mill.

At the mill, the seeds are deposited into the seed house by a bucket conveyor from the truck life or boxcar. Screw conveyors are not recommended for storage to avoid cracking or squeezing the seeds. The conveying systems throughout the plant require weekly cleaning to remove oil buildup. The seeds begin the extraction process by flowing

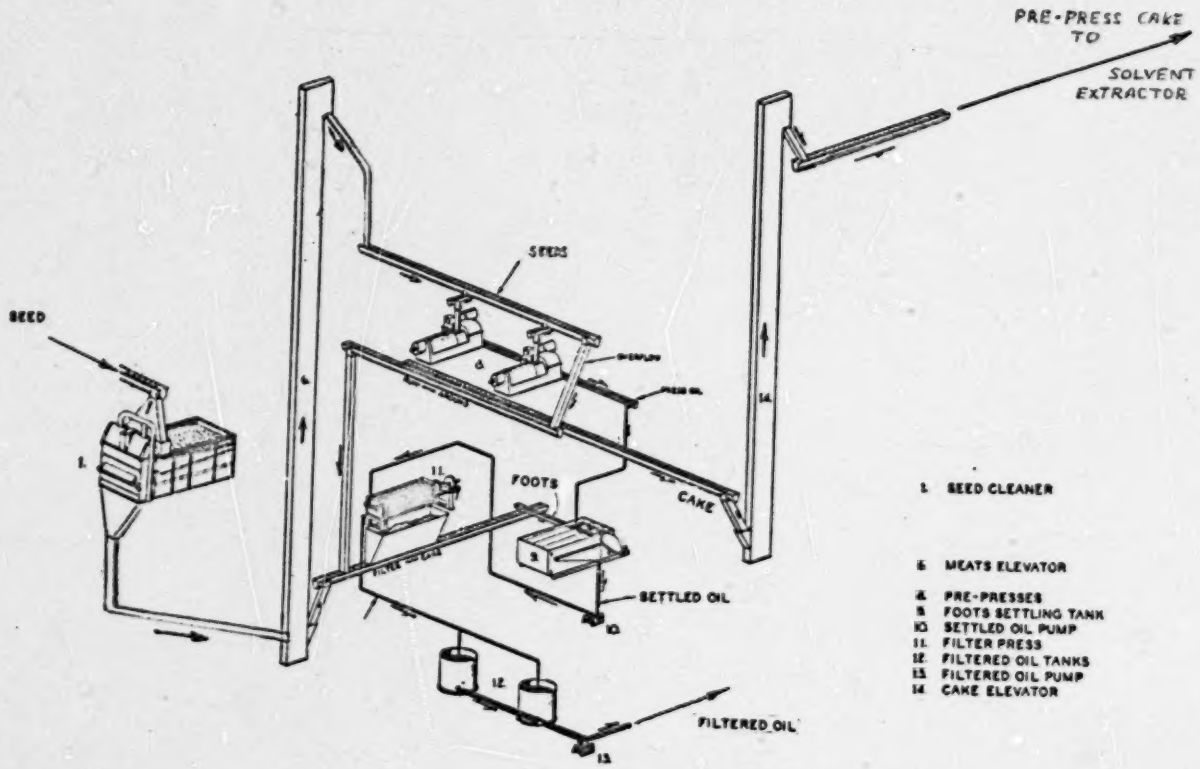
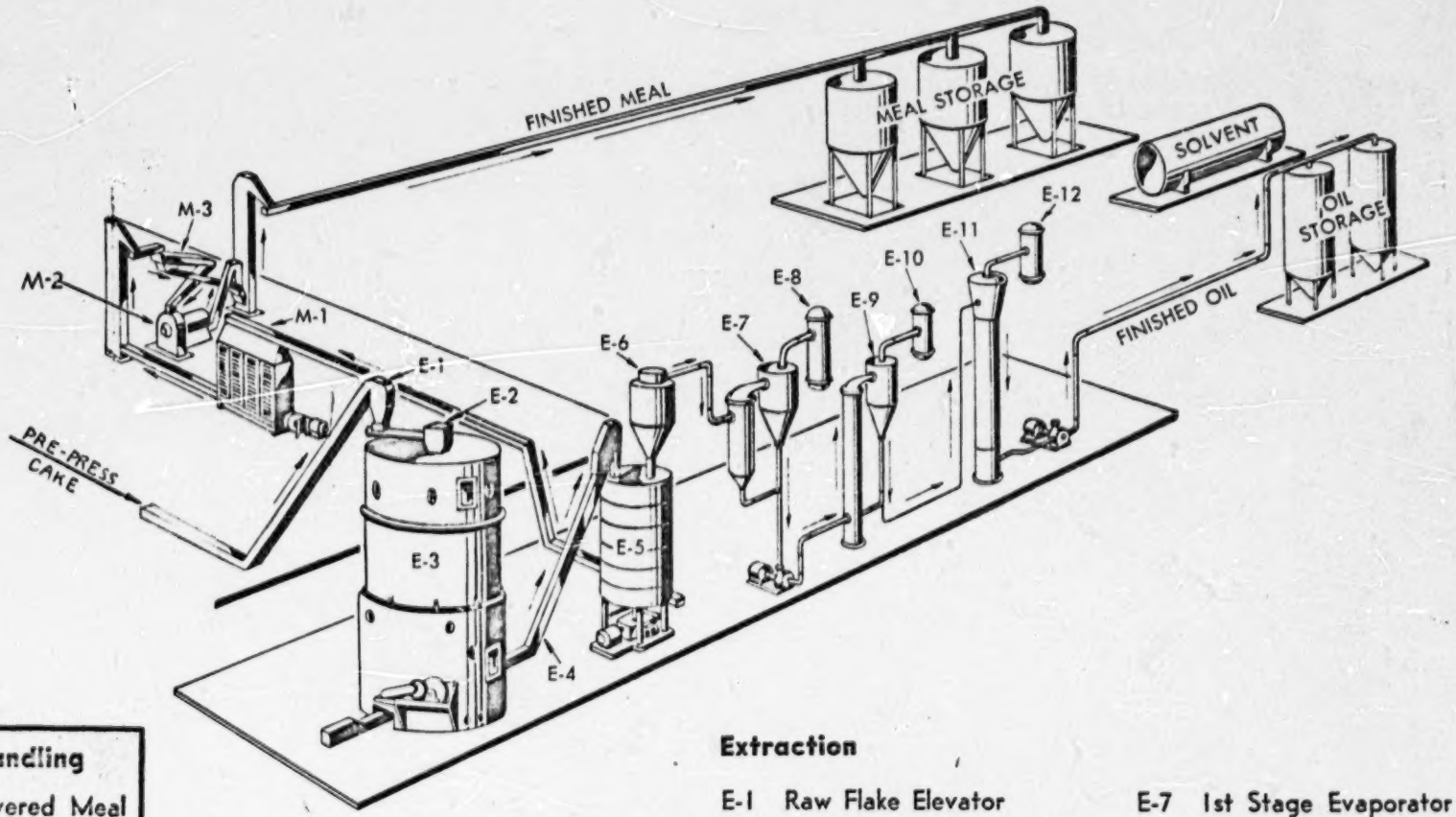


Figure 3-1. Pre-Pressing.



Meal Handling

M-1 Louvered Meal Cooler
M-2 Meal Grinder
M-3 Meal Screen

Extraction

E-1	Raw Flake Elevator	E-7	1st Stage Evaporator
E-2	Extractor Feed Conveyor	E-8	1st Stage Condenser
E-3	Stationary Basket Extractor	E-9	2nd Stage Evaporator
E-4	Spent Flake Elevator	E-10	2nd Stage Condenser
E-5	Desolventizer-Toaster	E-11	Final Oil Stripper
E-6	Vapor Scrubber	E-12	Vacuum Condenser

Figure 3-2. Solvent Extraction.

over a shaker cleaner and through a conditioner, raising the temperature to 210°F, at which point they enter the screw press [12].

3.2.1 Hydraulic Pressing

The hydraulic press, although considered obsolete, does produce a very pure, clear castor oil. The United States produced and used most of the hydraulic presses, and those in use abroad today are generally second-hard U.S. machines. Because it is a batch process, hydraulic pressing entails a higher labor cost than do the alternative methods of oil extraction. In addition, this method is less efficient in terms of oil recovery. The purer product is possible, however, with the hydraulic press because the seed undergoes less severe conditions of temperature and pressure [4].

Typically, the whole, cleaned seed is heated to 60-70°C and then pressed. The press cake (pomace) is then removed from the press. About two-thirds of the oil is removed in this operation. The remaining oil is usually removed by solvent extraction (which will be discussed below). The oil removed in this first step is called "No. 1 oil" and is a very clear, pure oil suitable for medicinal as well as industrial uses, whereas the oil removed in subsequent steps, "No. 3 oil," is a less pure, cloudy extraction suitable for industrial use only.

3.2.2 Screw Pressing

The majority of castor seeds (as well as most other oilseeds) are crushed in screw presses. The screw press allows for continuous operation and minimum labor requirements, however, the seeds undergo more severe conditions during the pressing operation, resulting in an oil containing more impurities than result from hydraulic pressing [4,13].

The extraction may be accomplished in a single pressing (removing up to 92 percent of the oil), or a portion of the oil may be extracted in a first pressing, with the remainder being obtained by either a second pressing or solvent extraction [4].

At the Plains Coop Oil Mill, the seeds are pressed to lower the oil content to 12 to 15 percent, after which a solvent extractor is employed. The oil obtained contains many protein foots which are removed by settling and centrifuging before bleaching. The bleaching earth and foots from the settling and centrifuging are discharged into the pre-press cake, all of which goes to the solvent plant [12].

3.2.3 Solvent Extraction

Solvent extraction is employed to remove the oil that remains in the pre-press cake. By bringing crushed or ground castor seeds into intimate contact with a hot petroleum solvent (such as hexane or heptane), virtually all of the oil remaining in the seed can be removed. For example, a pre-press cake containing 15 percent oil will contain only 1 percent after several hours of exposure to the hot solvent [4,13].

The Plains Coop uses a stationary basket extractor (French Oil Mill Machinery Co.), with hexane solvent. It is claimed by the mill that, using good undamaged seeds, the extracted oil from both the pre-press and the solvent extractor meet No. 1 castor oil standards [12].

3.3 CASTOR POMACE PROCESSING

A by-product of the oil extraction procedures is castor pomace, also called castor meal, equal in weight to about half that of the beans fed to the process. This is ground, dried, and stored in paper bags before shipment.

All of the harmful components of the castor seed are contained in this pomace. However, detoxification of the poisonous ricin is quite simple. Following extraction, moisture is added to the level of 15% by weight and the material held at about 200 F for three to four hours. In addition, the allergen potency may be simultaneously decreased as much

as a hundred-fold, but this may be no aid to sensitive individuals [7]. The allergen is similar to that contained in many common grains and seeds.

3.4 OIL REFINING

3.4.1 General

Because all castor oil is now imported, it would be very difficult to determine the production methods employed for U.S. raw material. An educated guess is that 10-15% is obtained by hydraulic pressing. Of the balance, most is screw-press oil and the balance from solvent extraction.

The extracted oil can be used as is or altered to meet the differing requirements of a variety of industries. Some of the unique and complex castor compounds that have been developed over the years are shown in Figure 1-1. Only those most commonly used are discussed here.

3.4.2 Dehydrated Castor Oil [14,15]

Dehydration is accomplished by heating castor oil in the presence of a suitable catalyst. The hydroxyl group combines with a hydrogen atom from an adjacent group to form water, thereby reducing a second double bond. Upon heating the castor oil to 180-230°C, any one of the following catalysts may be used: sulfuric acid, sodium sulfate, phosphoric acid, specially prepared tungstic acid, and phthalic anhydride. The result is an oil having marked drying powers, making it one of the few suitable substitutes for tung oil. The chemical reaction is given below.

$$\underset{\text{Ricinoleic acid}}{CH_3(CH_2)_5CH(OH)CH_2CH{:}CH(CH_2)_7COOH} \longrightarrow$$

$$H_2O + \underset{\text{9,12-Linoleic acid, 59-64\%}}{CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH}$$

$$+ \underset{\text{9,11-Linoleic acid, 17-26\%}}{CH_3(CH_2)_5CH{:}CHCH{:}CH(CH_2)_7COOH}$$

Some of the trade names for dehydrated castor oil include: castung, collanole, isoline, P.G.D. oil, synthenol, and synouryn.

3.4.3 Sulfated Castor Oil [13,14]

This product, also termed turkey red oil, requires both skill and experience to produce. Simply stated, reaction with sulfuric acid produces sulfation of the hydroxyl group, as well as secondary reactions. The actual reactions are very complex.

3.4.4 Hydrogenated Castor Oil [13]

By mixing castor oil with hydrogen under moderate pressure it becomes hydrogenated, resulting in a very hard fat with a melting point of 86°C. "Opalwax" is the trade name for a commercial brand of hydrogenated castor oil.

3.4.5 Blown Castor Oil [13,15]

The terms "bodied," "blown," polymerized," and "oxidized" are used interchangeably to describe castor oil that has been brought into intimate contact with air or oxygen at a temperature ranging from 80 to 130°C. The blown oil has a higher viscosity, specific gravity, and saponification value. The oil may be blown in open vats or in closed vats with vents. At elevated temperature this process produces a dense white smoke or fume. This emission is extremely irritating to the lungs and easily causes choking and coughing [16].

4. USES OF CASTOR PRODUCTS

4.1 OIL

The wide variety of castor oil uses can best be illustrated by the list of applications given in Table 4-1 [2]. Table 4-2 shows the applications of the more common oil derivatives.

Hydraulically-pressed oil is used principally for medicinal and cosmetic products (usually after de-odorization). Some is also employed for special hydraulic and lubricant purposes.

4.2 CASTOR POMACE

The major worldwide use for castor pomace is as fertilizer. The Florida citrus growers and Connecticut Valley tobacco farmers are the major domestic users. In the case of tobacco farmers, use appears at least partly to be based upon tradition [17]. The high cost of castor pomace plus the need to import future supplies, may cause a rapid decline in its use as a fertilizer.

An alternative use of castor pomace is as a cattle feed. The well-known toxic characteristics of the castor seed has inhibited ranchers from using the pomace even though research has shown it to be safe and effective if it has been detoxified [12]. Castor pomace is never used as a waste fuel domestically. The table below shows approximate end-use values of pomace [18].

Use	Market Value $/Ton
Feed	50
Fertilizer	12-25
Waste Fuel	3-4

TABLE 4-1. APPLICATIONS LIST FOR CASTOR PRODUCTS

- Acid Neutralizer (Scavenging)
- Adhesives
- Alcoholysis Catalyst
- Alkyds
- Aluminum
  - Foil Coatings
  - Paint Vehicles
  - Siding Finish
- Amino Resin Modification
- Anti-
  - Blocking
  - Bronzing
  - Corrosion Lubricants
  - Curtaining
  - Feathering
  - Floating
  - Flooding
  - Foam
  - Friction, Polypropylene
  - Misting
  - Rusting Lubricants
  - Static
  - Sticking, Resin Emulsions
  - Streaking
  - Syneresis
  - Tack, Butyl Rubber
  - Trailing
  - Wear, Lubricants
- Appliance Finishes
- Architectural House Paints
- Asphalt Compounds
- Athlete's Foot, powder/ointment
- Automotive Polish/Cleaner, emulsion
- Bactericide
- Belt Dressing
- Binders
  - Aggregate
  - Urethane
- Brake Fluids
- Calendering Aids
- Calks
- Can Coatings
- Candles
- Capacitors, Impregnants for
- Carbon Paper
- Catalyst: alkyds, polyesters
- Ceramic Slurries
- Chemical Intermediates
- Cleaning Compounds
- Clothing Interliner, Foam
- Coatings
- Color Chip Dispersions
- Color Dispersions
- Consistency Modification
- Copolymers
- Corrosion Inhibitors
- Cosmetics
- Coupling Agents
- Crayons
- Cutting Oils
- Defoamers
- Dielectric Compounds
- Dispersants:
  - Dye, Color, Pigment
- Dry Cleaning Compounds
- Duplicating Stencils
- Dye Carrier
- Elastomers, urethane
- Emollient
- Emulsifiers
- Emulsion Additives
- Enamels
- Encapsulants
- Epoxy Esters
- Epoxy Modifiers
- Exempt Solvents
- Exterior Latex Paints
- Extrusion Aids
- Factice
- Filter Foams
- Flavor Intermediates
- Flexible Lacquers
- Flexible Foams
- Flocking Adhesive
- Flooding, Floating and Bronzing
- Floor Coverings
- Flushing Vehicle, Inks
- Foams (rubber; urethane)
- Food
  - Color, solvent
  - Machinery Lubricant (FDA)
  - Packaging
- Functional Fluids
- Fungicide
- Furniture Polish/Cleaner, Emulsion
- Gasket Compounds
- Germicides
- Glazes
- Grease
- Greaseproofing
- Hair Preparations
- Hot Melts
- Hydraulic Fluids
- Impregnants, Urethane
- Injection Molding Aids
- Inks
- Insecticide
- Internal Lubricants:
  - Plastic; rubber
- Investment Casting
- Isocyanate Reactants
- Lacquers
- Laminants
- Latex Paint Additives
- Leather Coatings
- Leveling and Brushability
- Lipsticks
- Lithium (Calcium) Greases
- Low Temperature Plasticizers
- Lubricants
- Mastics
- Meat Packaging Film
- Mold Release Agents
- Motor Fuel, additive for
- "Nerve" Reducer, Rubber
- Oiliness Agents
- Ointments
- Packings, mechanical
- Paints
- Paper Coatings
- Penetration Control
- Perfume Intermediates
- Pesticides
- Pharmaceuticals
- Phenol Coefficient Synergizer
- Phenolic Resins
- Pigment Dispersion
- Pigment Suspension
- Plasticization
- Plastics, Reinforced
- Plastisols
- Plug Valve Grease
- Polishes
- Polyamide Plastics
- Polyesters
- Post Additive, flow control
- Potting Compounds
- Primer: Ethylene/Propylene Rubber
- Processing Aids
- Putties
- PVC (Rigid) Processing
- Resins
- Rubber
- Rubber Accelerator
- Rubber Cement and Solutions
- Rubber Compounding
- Rubber Preservatives
- Rust-Proof Agent
- Sag and Slump Control
- Sealants
- Shampoos
- Shock Absorber Fluid
- Shock Absorbing Elastomers, Foams
- Slip Agent (Varnishes, Lacquers)
- Soaps
- Solubilizers
- Sonar Fluid
- Stabilizers
- Stains
- Strippable Coatings
- Sulfonation
- Tack Rags
- Tackifiers
- Textiles
- Thixotropes (Rheological Agents)
- Traffic Paints
- Troweling Compositions
- Transducer Fluid
- Universal Colorants
- Urethane Adhesives
- Urethane Binders
- Urethane Cast and Molded Goods
- Urethane Coatings
- Urethane Elastomers
- Urethane Floccing Adhesives
- Urethane Foams
- Urethane Impregnants
- Urethane Potting Compounds
- Urethane Sealants
- Varnishes
- Vehicle Ink
- Vinyl Compounding
- Vinyl Resins, Stabilizers
- Vinyl-Urethane Coating
- Viscosity Control
- Water-Proofing
- Wax Blends
- Wax Polishes
- Wax Substitutes
- Wetting Agent
- Wire Drawing Compounds
- Wire Enamels
- Wood Fillers
- Yarn Dressings

TABLE 4-2

APPLICATIONS OF SPECIAL CASTOR OIL DERIVATIVES

Type of Product	Applications
Blown Castor Oil (polymerized oils)	Adhesives Floor coverings Lacquers Lubricants "Nerve" reducer, rubber Pigment dispersion Plasticization Resins Viscosity Control
Refined Castor Oil	Alkyds Adhesives Cosmetics Hydraulic Fluids Inks Isocyanate reactants Laminants Lubricants Mold release agents Rubber preservatives
Dehydrated Castor Oil (drying oils)	Alkyds Calks Copolymers Enamels Oil-based paints Putties Resins Varnishes Traffic paints Ink vehicles Wire enamels Aluminum siding finish Aluminum paint vehicles Phenolic resins
Fatty Acids	Bactericide Copolymers Corrosion inhibitors Cosmetics Cutting oils Epoxy esters Flavor intermediates Foam rubber

TABLE 4-2 (continued)

Type of Product	Applications
Fatty Acids (continued)	Fungicides Germicides Grease Inks Perfume intermediates Pharmaceuticals Polishes Polyamide plastics Resins Soaps Wax blends
Hydrogenated Oil (hydroxy waxes)	Candles Cosmetics Crayons Food packaging Grease Hot melts Impregnants Inks Investment casting Mold release agents Paper coatings Pharmaceuticals Polishes Potting compounds Sealants Slip agent Wax blends

5. INDUSTRY EMISSIONS

5.1 PARTICULATES

The emission of particulates may occur during the handling of the seed before processing, and in the handling and use of the castor pomace after processing. Particulate emission rates have never been quantified and the lack of domestic cultivation and crushing makes such future testing unlikely. As an alternative, a study of emissions from similar oilseeds may yield a valid approximation.

The particulates emitted contain some of the toxic components of the castor seed, especially the emissions that occur before processing, since, at this stage, the ricin cannot yet be detoxified. Also, as has been well documented [19], handling the castor seed can result in allergenic reactions due to the dust; this can occur during harvesting, transportation, conveying, etc.

It has been related to us that when the Plainview Coop was being established, it was deliberately located downwind and somewhat remote from the nearby town. During their period of operations, the only complaints due to allergenic dust came (occasionally) from the single home nearest to the plant.

5.2 EMISSIONS FROM OIL REFINING

In most respects, the emissions from castor oil refining processes are similar to those encountered in the processing of other vegetable oils. Unlike the particulate emissions, the oil emissions are non-toxic, increasing the similarity with other vegetable oils.

Baker, Pacific and Spencer Kellogg all "blow" castor oil and incinerate the off-gases, the first two in afterburners, the last in their boiler. Spencer Kellogg also carries out dehydration (at approximately 500 F), scrubbing the exhaust gases. Degen makes alkyd resins by esterification but by employing reflux operations with a solvent, claims to have no atmospheric emissions.

Table 2-1 indicates that the above discussion includes most of the high-temperature processing of the castor oil itself.

6. BEST CONTROL

6.1 TECHNOLOGY

6.1.1 Dry Particulate Collector

The collection of particulate emissions can be accomplished through the use of a fabric filter (or baghouse). This would be feasible wherever the emission source was sufficiently localized to permit hooding. For example, hooding would be necessary at the seed unloading areas, and at the shaker cleaner locations. The castor pomace bagging facilities would also need hooding. All such sources could be ducted to a central processing plant where a fan would provide motive power. Shutoff devices (butterfly valves) would allow selective application of the air cleaning equipment. Design should provide for velocities of approximately 150 fpm through the hood opening to be effective in preventing escape of dust. Fabric selection can be tailored over a broad range according to process requirements and collection efficiency of 99.9% or greater can be achieved.

6.1.2 Wet Scrubbers

A major drawback with the employment of wet scrubbers on dust collection is the introduction of a water pollution problem.

For treatment of hydrocarbon and odors, research findings [20] stated "performance ... limited to removal of fumes condensed by or dissolved in the wash water ... operating with water as the washing agent does not and cannot remove those gases which are major odor producers." Nothing in more recent work, in this or any other field of odorous gases indicated a different conclusion -- whether on low pressure scrubber devices, packed towers or high pressure venturi scrubbers.

Supplementing the performance of the wet scrubbers by means of additives is a very distinct possibility and has been employed successfully in some fields -- rendering plants, for example. The additive is any of several possible oxidizing agents such as potassium permanganate, or calcium or sodium hypochlorite, or others.

One of the potential problems here is that this scheme has been known to be effective in overcoming known emissions odors but at the same time has been responsible for the generation of new and equally potent malodors. It is a system that must be piloted carefully before applying to a full-scale commercial operation.

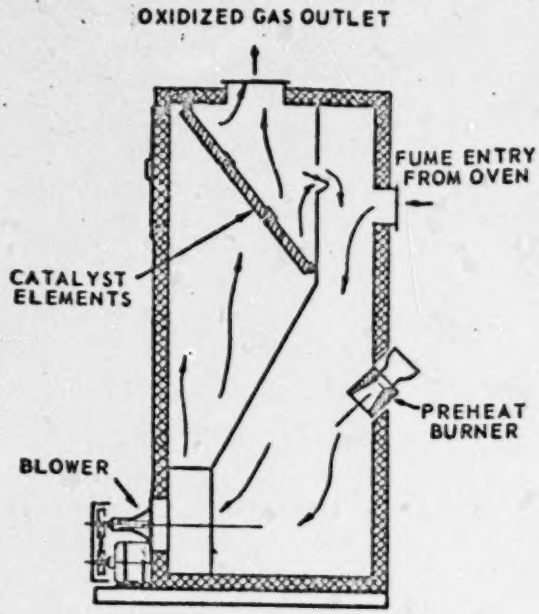
6.1.3 Adsorption

Installation of equipment for adsorption of odors on activated carbon is a process that is successfully employed on solvent vapors (such as dry cleaning plants) and similar operations. Although a possible control method for organic emissions from oil processing, it is very unlikely that it is being applied commercially.

6.1.4 Incineration

Incineration of organic gases has generally been accepted as the one certain method for elimination of organic compounds and their associated odors. During proper incineration all carbon and hydrogen oxides become harmless, non-regulated carbon dioxide and water vapor. Thus, organics and/or hydrocarbons are, by definition, non-existent and odor is no longer possible. Resulting water vapor, even if visible, is specifically exempt under even the most stringent regulations. Three schemes for incineration are possible and are outlined below.

6.1.4.1 Catalytic oxidation. The offending gases and vapors are collected and blown to the equipment wherein they are heated, by combustion of fuel, to the range of 600-800°F. They are then passed through a catalyst bed which is usually an inexpensive base material coated with a precious metal. The catalyst causes a further temperature rise due to oxidation of the hydrocarbons. The disadvantages of catalytic units are: (1) they are more expensive from a capital investment standpoint than other incineration equipment, (2) it is possible that contaminants in the gases can "poison" the catalyst, rendering it ineffective and requiring its replacement, and (3) it has occasionally been observed that catalytic units, while destroying most of the contaminants, generate new compounds which have their own obnoxious odor characteristics.

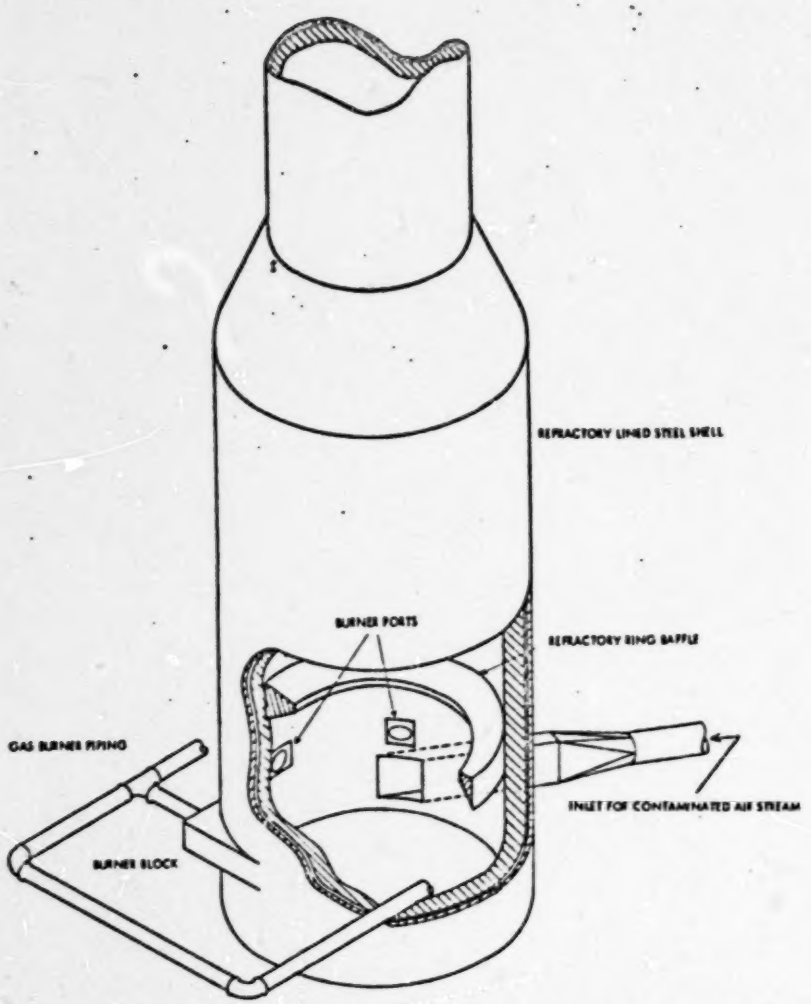


Catalytic afterburner. (Courtesy Catalytic Combustion Corporation)

6.1.4.2 Thermal incineration requires that the same oxidation process as above proceeds in the presence of higher temperature generated by fuels or the combustible content of gas itself. The general requirements are that the temperature be in the range of 1200-1400°F and the residence time between 1/4 and 1/2 second [21]. Also stressed by some are such factors as turbulence and mixing. The temperature may be raised to this level by introduction of combustion gases, by heat exchange or other means. (Some report the necessity of going as high as 1500°F.)

6.1.4.3 Flame, or fume, incineration is very closely allied to the above method. The difference is that the contaminated gases pass through the flame by forcing mixing or, better, are employed as part or all of the source of combustion air. The same parameters of time and temperature are indicated by some, but others feel that flame incineration, with its temperatures of 2000-2500°F, implies virtually instant

oxidation -- as indeed it is for the hydrocarbons of the fossil fuel which, under proper combustion conditions, are completely oxidized to CO_2 and H_2O. Because of the higher temperatures involved, flame or thermal incineration have greater fuel requirements and, therefore, higher operating costs than a catalytic unit. However, they do not incur the risk of catalyst poisoning nor the cost of catalyst replacement after a period of time.



Vertical gas-fired afterburner with tangential entries for both the fuel and contaminated air.

6.2 TYPICAL CONTROLLED INSTALLATIONS

According to a source at the Spencer Kellogg Company (the second largest oil refiner), the only pollution problem they have is an odor problem, for which they use masking chemicals [22]. When beans were processed at their plant, in the past, cyclones and fabric filters were used to control dust.

The largest castor oil refiner is the Baker Castor Oil Company, whose Bayonne, New Jersey plant was visited by Walden Research and EPA personnel. Their blown oil operation emissions are controlled by an incinerator manufactured by Hirt Combustion Engineers, Model HIH-4600X. The unit has a design capacity of 4,600 scfm of "diluted" off-gases from eight castor oil cooling kettles. Hirt has test data on the unit indicating hydrocarbon discharge of less than 100 ppm when the unit is operated at 1400°F and with maximum inlet hydrocarbon loading. The unit is a high induced draft fume incinerator [22,23].

The Plains Coop Oil Mill uses fabric filters to control dust generated in the storage area. The fertilizer companies also report the use of bag filters in their mixing areas to control the castor pomace dust [24].

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